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TRENDS IN CONCENTRATIONS OF BENZENE-SOLUBLE SUSPENDED PARTICULATE FRACTION AND BENZO(a)PYRENE

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Environmental Protection Agency
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This special report continues EPA's effort to document trends in existing data from the National Air Surveillance Network as well as other State, county, and local air monitoring programs. Previously, reports have dealt mainly with trends in pollutants for which National Ambient Air Quality Standards (NAAQS) have been set. However, EPA recognizes the need to examine other pollutants for which the NAAQS have not been set so that an assessment can be made of the seriousness of the air pollution problems associated with these substances. In this report the existing data on the benzene-soluble fraction of the total suspended particulate measurement and benzo(a)pyrene a constituent of this fraction are examined for trends, and other relationships.

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1. Correct title for Table 3-1 to read: Distribution of Spearman Rank Correlation Coefficients of BSO (1960-1970) versus Time for Urban and Nonurban NASN Sampling Sites.

2. Correct title for Figure 3-8 to read: BaP 1968-1970 Rounded Average for NASN Stations Having Complete Data for the 3-Year Period Considered and 1970 Bituminous and Lignite Coal Distribution by State.

3. Correct heading in Figure 3-9 to read:

   BENZENE-SOLUBLE ORGANICS
   ($\mu g/m^3$)

4. Add YEAR below numbers along x axis in Figure 3-10.

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ABSTRACT

This special report continues EPA's effort to document trends in existing data from the National Air Surveillance Network as well as other State, county, and local air monitoring programs. Previously, reports have dealt mainly with trends in pollutants for which National Ambient Air Quality Standards (NAAQS) have been set. However, EPA recognizes the need to examine other pollutants for which the NAAQS have not been set so that an assessment can be made of the seriousness of the air pollution problems associated with these substances. In this report the existing data on the benzene-soluble fraction of the total suspended particulate measurement and benzo(a)pyrene a constituent of this fraction are examined for trends, and other relationships.

LIST OF ABBREVIATIONS

BaP	Benzo(a)pyrene
BSO	Benzene-Soluble Organic Fraction of the TSP
NASN	National Air Surveillance Network
PAH	Polycyclic Aromatic Hydrocarbons

UNITS

ug/m^3	Micrograms (grams x 10^{-6}/meter^3
Ng/m^3	Nanograms (grams x 10^{-9}/meter^3

1. SUMMARY

1.1. Introduction

This paper presents national trends in the benzene-soluble portion (BSO) of total suspended particulate matter in ambient air for 1960 through 1970 at 126 urban and 25 nonurban sites. Additionally, trends for benzo(a)pyrene (BaP), a polynuclear aromatic hydrocarbon (PAH) present as a component of the BSO fraction, will be presented for 1966 through 1970 at 126 urban and 22 nonurban stations. Analyses of BaP and BSO data were also made for 33 urban locations for which data was available for 1971 and 1972. Currently, data are not available for other PAH compounds and organics making up the remainder of BSO. Analysis of BSO and BaP and other important organic particulates are needed on a routine basis across the country as well as more intensified studies in urban areas where these pollutants are possible hazards. This report in addition to highlighting trends will also identify areas where above average ambient concentration of BSO and BaP are found.

1.2. Trends in Benzene-Soluble Suspended Particulate Fraction and Benzo(a)pyrene.

Ambient concentrations of BSO decreased significantly nationwide for urban stations from 1960 to 1970. The composite average of 32 urban stations for which complete data was available dropped consistently from 10.6 ug/m^3 in 1970 to 4.8 ug/m^3 in 1970. Out of 126 urban stations studied, 118 exhibited negative-rank correlations with time, indicating the tendency at these stations of a decreasing trend in BSO concentrations. At more than half of the stations studied BSO showed a statistically significant downward trend.

Decreases in urban BaP concentrations were also observed, but, the limited data available prohibit a statistical evaluation of this change. The composite BaP average of the 32 urban stations dropped about 30 percent from 1966 to 1970. The decreasing trends in BSO and BaP appear to be continuing for the 33 sites with data available for 1971 and 1972.

The nonurban stations for BSO do not show an apparent trend for the period 1965-1970. However, since 1966 the composite average has dropped from 2.2 ug/m^3 to 1.2 ug/m^3 in 1970. A very slight decline in the non-urban BaP composite average has also been found.

The estimated national consumption of coal by small consumers for heating purposes decreased approximately 50 percent in the 1960-70 period, and this decreased use during this period is probably the principal factor contributing to the trends in BSO and BaP. A similar percentage decrease was observed in composite average BSO concentrations for urban stations. Local open-burning ordinances and controls on automobiles instituted during this period are other possible factors contributing to the observed trends for these suspended particulates.

2. INTRODUCTION

2.1. General Background

Recent studies[1] of data obtained through the operation of the National Air Surveillance Network (NASN) have shown that atmospheric concentrations of sulfur dioxide and total suspended particulate matter (TSP) are on the decline in most urban areas. The purpose of this paper is to examine trends in concentrations of benzene soluble organics (BSO) and benzo(a)-pyrene (BaP), two other pollutants monitored through the operation of NASN.

The polycyclic aromatic hydrocarbons (PAH), many of which are present in the BSO fraction, have been linked to cancer in animals.[2,3] Benzo(a)pyrene, a PAH that is present in the BSO fraction, is believed to be potentially carcinogenic in man.

2.2. National Air Surveillance Network

The National Air Surveillance Network (NASN) has been in operation since 1957 and has been administered by a number of Federal agencies responsible for monitoring important air pollutants on a nationwide basis. Under NASN, approximately 250 high-volume samplers are maintained annually in the major American cities and selected rural areas. Twenty-four-hour samples are taken biweekly at each of the monitoring stations. After collection, the samples are forwarded to a central laboratory for gravimetric and chemical analyses of the suspended particulates. Since 1964 the organic analysis has been done by compositing individual samples by quarter to save both time and expense of the analysis.

For measurement of the benzene-soluble fraction, the sample is extracted with redistilled benzene in a Soxhlet extractor for 6 hours. Removal of the solvent leaves the dissolved organic material as a residue. BaP is determined by separating the extracted organic material into its different components by thin-layer chromatography and the removal of the BaP from the thin-layer absorbent. The BaP is then dissolved in sulfuric acid and its concentration is measured by fluorescence spectroscopy.

The urban NASN sampling sites were chosen to generally be representative of the downtown business districts in their respective cities. On the other hand, nonurban sites are generally located in Federal or

State parks removed to a great extent from the direct impact of man. Data from these sites either provide estimates of background concentrations of the organic particulates released near the site from man-made or natural sources, or they may be a function of long-range transport phenomenon from urban areas. The difference between urban and nonurban concentrations provides a gross estimate of the effect of the varied urban pollution sources on concentrations of these organic suspended particulates.

2.3. Report Limitations

The last year that routine NASN BSO and BaP data exist is 1970, although 1971 and 1972 is available for a selected group of 33 NASN sites. It is unfortunate that more recent data is not available so that more up to date trends could be ascertained. The BaP data is further limited because its analysis began on a network basis in 1966. Furthermore, data on other important and possible hazardous hydrocarbons present in the BSO fraction are nonexistent.

The data reported herein represent a single sampling site per urban or nonurban area. As a result, they do not provide an adequate picture of concentrations in other portions of the metropolitan area. Organic particulate data for multiple-site networks within a metropolitan area are just now becoming available, and future reports on this subject can study trends across the entire urbanized area.

It was not possible for much of the data to factor out or explain the year to year variation in concentrations caused by meteorological or other extraneous factors which influence particulate loadings and more specifically the organic particulates on a given day because the data

existed as quarterly composited values only.

3. TRENDS IN ORGANIC FRACTIONS OF TOTAL SUSPENDED PARTICULATES

3.1. Methodology

Two distinct approaches were used to show the trends in BSO and BaP concentrations. The first method, which is strictly descriptive, was used to show general or national trends and is based on comparisons of the composite stations averages over the period from 1960-1970. Unfortunately, the number of stations reporting valid consecutive annual data differed widely during the period. For example, 157 urban sites had data for BSO in both 1969 and 1970, whereas data were available for only 50 urban sites in the interval 1965-1970. To eliminate the possibilities of bias, the analysis of BSO and BaP trends was limited to those stations for which data are available for every year from 1960 through 1970. In a few rare cases, annual averages were computed based on only 3 valid quarters of data to preserve the continuity of a data record. Because of the inherent seasonality present in the data, this could lead to erroneous averages, but this occurred so infrequently that there was minimal effect on the analysis of the data. Thirty-two urban stations satisfied the criteria for BSO. However, the BaP analysis for this same set of stations is restricted to the shorter interval of 1966-1970 because pre-1966 BaP do not exist. Additionally, data from 19 nonurban stations are summarized for BSO and BaP, respectively, over the intervals 1965-1970 and 1966-1970. Quarterly composite averages for these same sites are presented to show the seasonal effect on concentrations and trend patterns. Appendices A and B to this report provide a listing of the

stations used in this composite analysis and a brief description of the overall trend observed at each of the urban and nonurban stations.

A second form of anlaysis was employed to expose trends at individual stations. This was accomplished by utilizing the Spearman rank correlation coefficient as the test statistic. The Spearman coefficient measures the strength of the association between the annual arithmetic average of BSO and BaP and time. It has the same properties as the common product-moment correlation coefficient, that is, a positive coefficient indicates a direct association (an upward trend), while a negative coefficient indicates an inverse association (a downward trend). The closer the coefficient is to ± 1, the stronger the association between the pollutant concentration and time and thus, the stronger the trend. A two-sided statistical test at the 5-percent level was used to determine the significance of the individual station trends. Although it was previously noted that data are unavailable for some years at some stations, 126 urban and 25 nonurban stations have sufficient data for the analysis of BSO trends by this technique. The same number of urban stations and 22 nonurban stations had sufficient data for BaP trends evaluations.

3.2 Trends in Benzene-Soluble Organic Suspended Particulate Fraction

3.2.1. National Urban and Nonurban Trends

Composite annual averages of BSO concentrations and BSO expressed as a percent of TSP are shown in Figure 3-1 for the 32 urban and 19 nonurban NASN stations. The urban composite average concentration of BSO has decreased from 10.6 ug/m^3 in 1960 to 4.8 ug/m^3 in 1970. This represents a 55 percent decrease. The trend in BSO concentrations shown closely parallels the trends observed at the vast majority of the stations included in the composite sample. Statistically downward trends were found for 27 out of the 32 stations represented by this grouping. Only in Helena, Montana, was there some indication found of an increasing trend pattern. Portland, Oregon, did not exhibit a clear-cut trend pattern and was described as having "no trend," whereas Providence, Rhode Island, Seattle, Washington, and Milwaukee, Wisconsin, exhibited weaker decreasing trend patterns than was the general case. The overwhelming consistency in trend patterns points to some general phenomenon exclusive of geographical location within the country, city size, or industrial sources present in a particular city.

The decrease in the composite average concentrations of BSO in 1963 -- approximately 1 ug/m^3 -- together with similar decreases in 1964 and 1970, represent the years with the largest concentration changes. The nonurban average BSO concentration, which is a factor of approximately 4 or 5 less than the urban averages, exhibits a more uncertain pattern. However, since 1966, nonurban BSO averages have decreased from 2.2 ug/m^3 to 1.2 ug/m^3 in 1970.

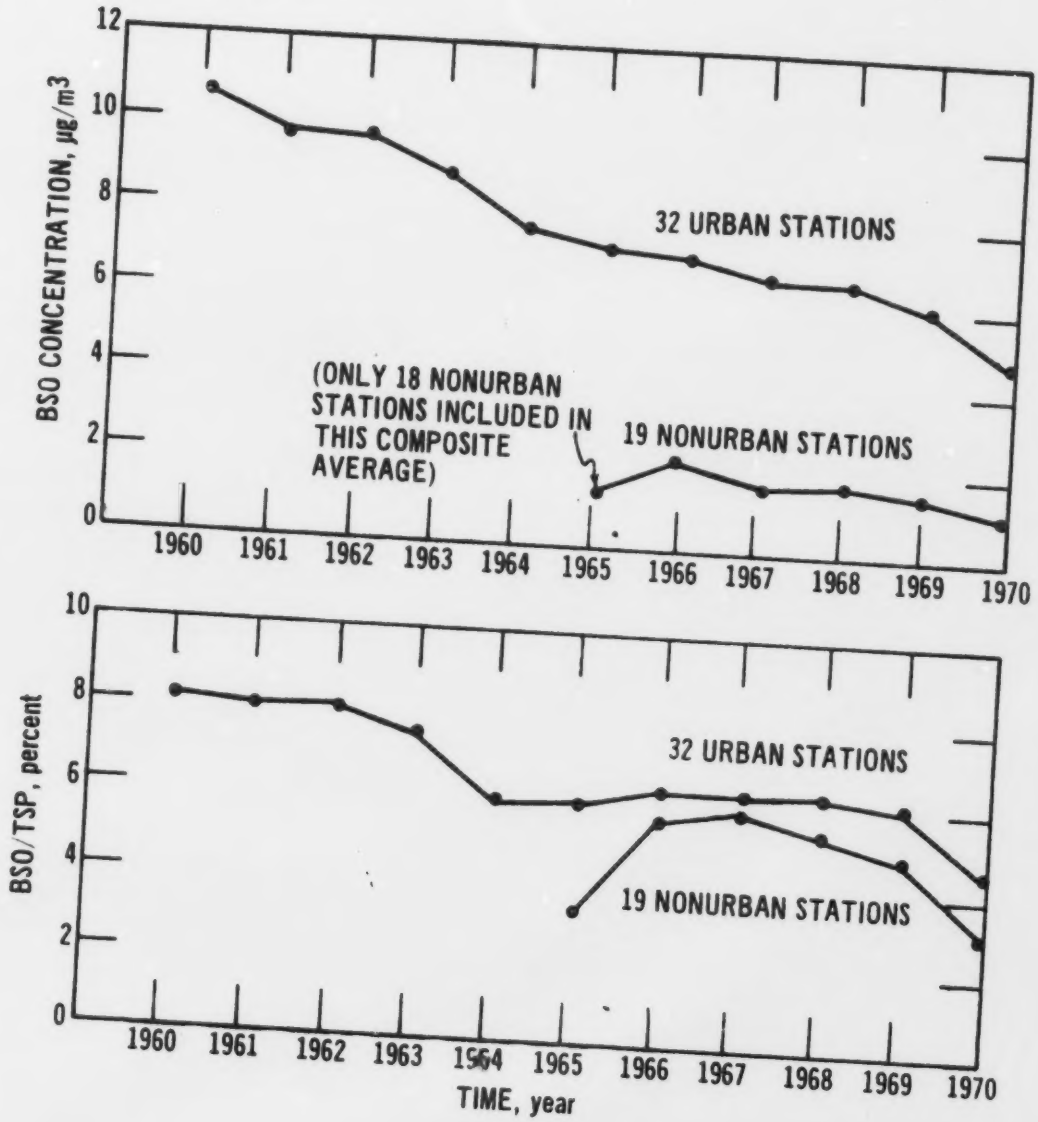

Figure 3-1. Trends in BSO and BSO percent of TSP at 32 urban and 19 nonurban stations.

The BSO percent of TSP has also decreased for the urban stations over the period considered. The pattern is characterized by rather sudden decreases from 1963 to 1964 (8 to 6 percent) and from 1969 to 1970 (6 to 4.5 percent). In other years, the BSO percent of TSP remained relatively constant. It appears that significant decreases in national urban levels of both BSO and BSO percent of TSP have occurred, notwithstanding sizable, short-term, year-to-year fluctuations.

It is interesting to note that the averages of the BSO concentration and the BSO percent of TSP for the nonurban stations (with the exception of Curry County, Oregon) were lower in 1965 and 1966. However, insufficient pre-1965 data exist to judge whether trends in nonurban BSO concentrations have paralleled the concentration decreases at the urban sites.

In a statistical approach to this study of National Trends in BSO, data from individual stations were tested for trends using the Spearman Rank Correlation Coefficient described to a limited extent earlier. Recall that positive and negative coefficients indicate possible upward or downward trends, respectively, with the strength of the association increasing the closer the coefficient is to ± 1.

For all urban stations, the coefficients (rank correlation) of BSO are predominatly negative. Of the 126 stations studied for BSO, 118 had negative correlations with time. Seventy-five stations of the 118 with negative correlations had coefficients that were statistically significant at the $\alpha=0.05$ level. A statistically significant coefficient implies that

it is unlikely that the observed rank correlations coefficients were derived from a population whose true correlation was zero. In the case of a significant coefficient, we can infer that a significant association exists between BSO and time and, therefore, conclude that the available evidence supports a negative or downward trend in annual average concentrations at these 75 stations. Table 3-1 shows the distribution of the individual station Spearman Correlation Coefficients by catagories of sign and strength for BSO.

Correlations involving certain quarters over the period were performed independently (the correlations of the first quarter with time, second quarter with time, etc.). These correlations for BSO indicated basically what has been observed before. The coefficients for the heating quarters were predominantly negative and, in most cases, were approximately the same as the correlations presented earlier of the annual average versus time. The correlations for the non-heating quarters again were mostly negative, but the associations were generally not as strong as for those quarters having a heating demand.

Four nonurban stations two in the west (Butte County, Idaho, and Curry County, Oregon) and Indiana (Monroe County and Parke County) had significant downward trends, Overall 15 of the 25 nonurban studied had negative rank correlation coefficients.

Table 3-1. Distribution of Spearman Rank Correlation Coefficients of BSO (1960-1970) Time for Urban and Nonurban NASN Sampling Sites

Spearman Rank Correlation Coefficient Categories	Benzene Soluble Suspended Particulate Fraction	
	Urban Sites	Nonurban Sites
-0.81 to -1.0	56 (55)*	2 (2)
-0.61 to -0.80	39 (20)	2 (2)
-0.41 to -0.60	13	2
-0.21 to -0.40	8	5
<0.00 to -0.20	2	4
0	1	1
>0.00 to +0.20	3	3
+0.21 to +0.40	1	2
+0.41 to +0.60	2	2
+0.61 to +0.80	2	
+0.81 to +1.00	0	0
TOTAL	126 (75)	25 (4)

*Numbers in Parenthesis refer to the number of stations per category having Spearman Correlation Coefficients significantly different from zero at the $\alpha = 0.05$ level of significance.

3.2.2. Seasonal Trends

Figure 3-2 depicts the composite quarterly BSO averages for the 32 urban and 19 nonurban stations. The seasonality in urban BSO is very pronounced (especially for the first half of the data record), with the heating months (first and fourth quarters) showing averages that are 1.5 to 2 times the mean of the second and third quarters. The fourth quarterly average has decreased from 13.5 ug/m^3 (1960 heating season) to 7.7 ug/m^3 (1970 heating season), a decrease of approximately 43 percent. The decrease in the heating season's average BSO concentration closely parallels the overall decrease in the annual average shown earlier.

The year to year variation in the average composites for the second and third quarters shows three possible distinct downward shifts. These shifts occur at the beginning (1960-1961), in the middle (1963-1964) and the end (1969-1970) of the 11 year period under consideration. Sizeable BSO to TSP percentage decreases were also found for the middle and end drops. At the present time no explanation can be found for the stepwise summer BSO pattern for many NASN urban sites across the nation.

The nonurban stations show a less pronounced and regular seasonal pattern for BSO than the urban stations. Generally the averages of the first and fourth quarters are the highest. The 1970 composite quarterly averages appear atypical, having generally lower concentrations and less variability than prior years.

Figures 3-3 and 3-4 show the seasonal patterns in BSO and BaP at the Albuquerque and Cleveland NASN sites. These data are presented to point out

that all urban sites such as Cleveland do not show a seasonality for these pollutants. The lack of seasonality for the Cleveland site could possibly be the result of industrial sources of BSO and BaP operating year around, e.g., the production of coke. The BSO and BaP data from Albuquerque exhibit a very regular seasonal pattern (fourth quarter usually the highest) and decreasing trends.

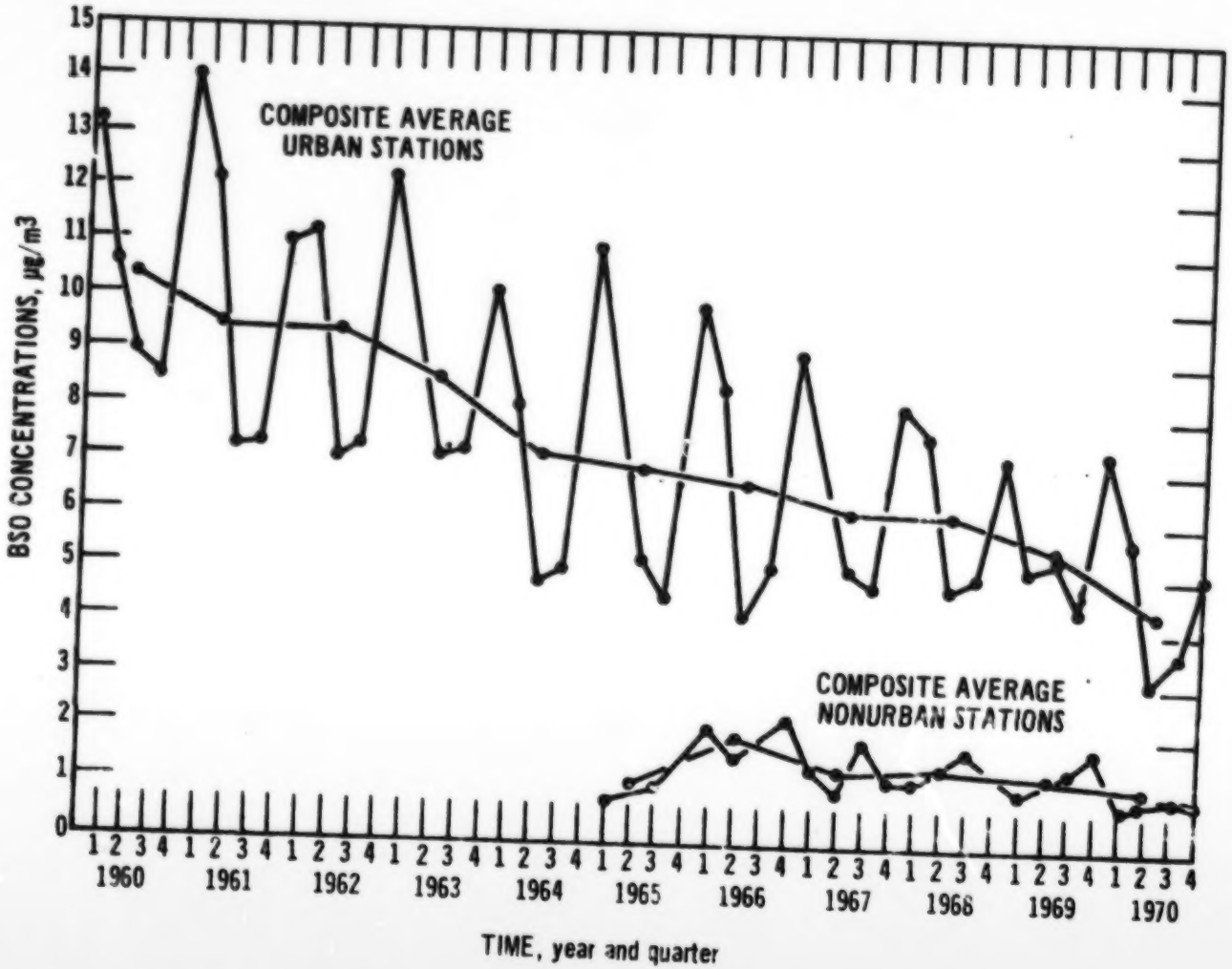

Figure 3-2. Composite quarterly averages for BSO at 32 urban and 19 nonurban NASN stations.

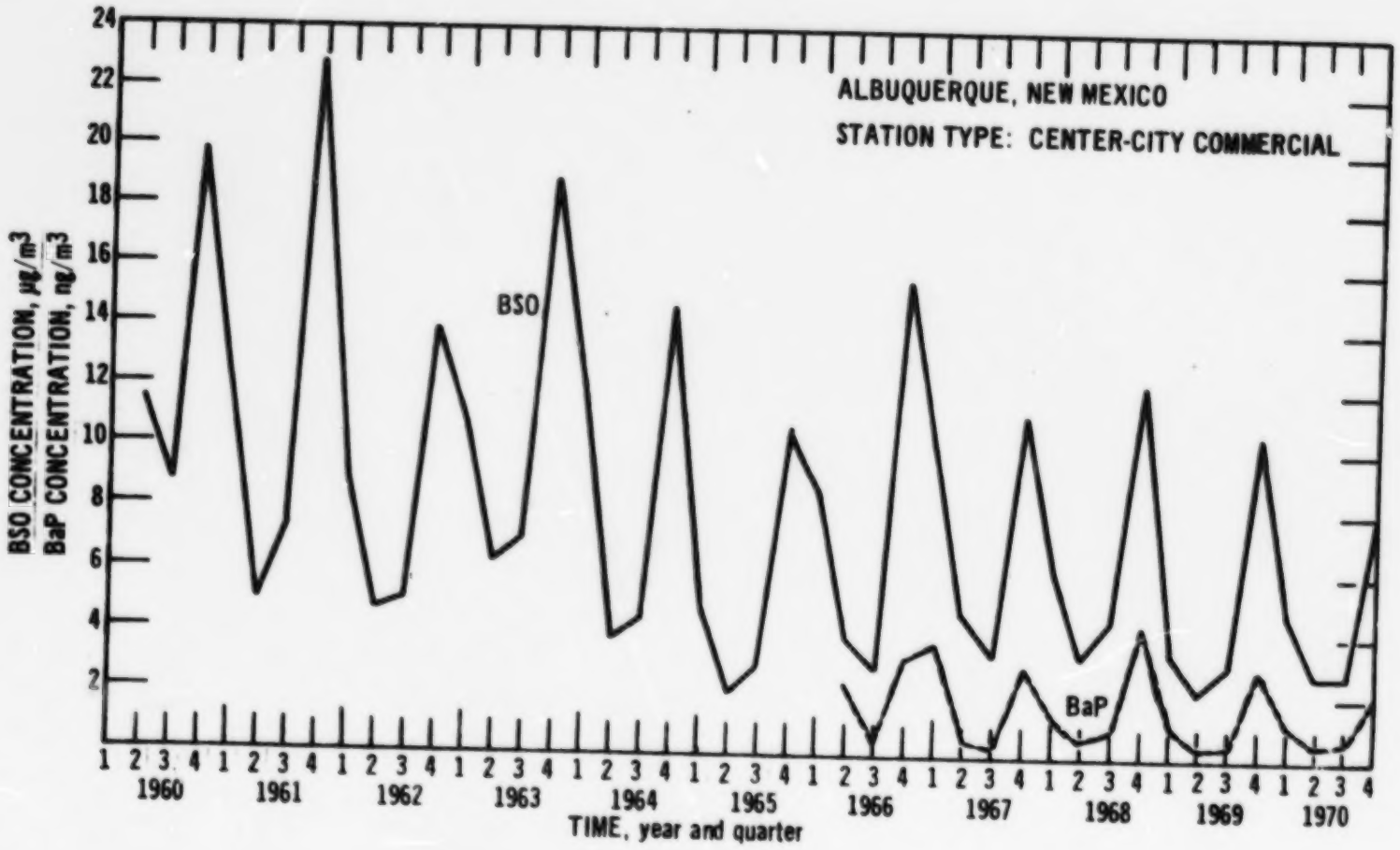

Figure 3-3. Quarterly averages of BSO and BaP at the Albuquerque, New Nexico NASN Station.

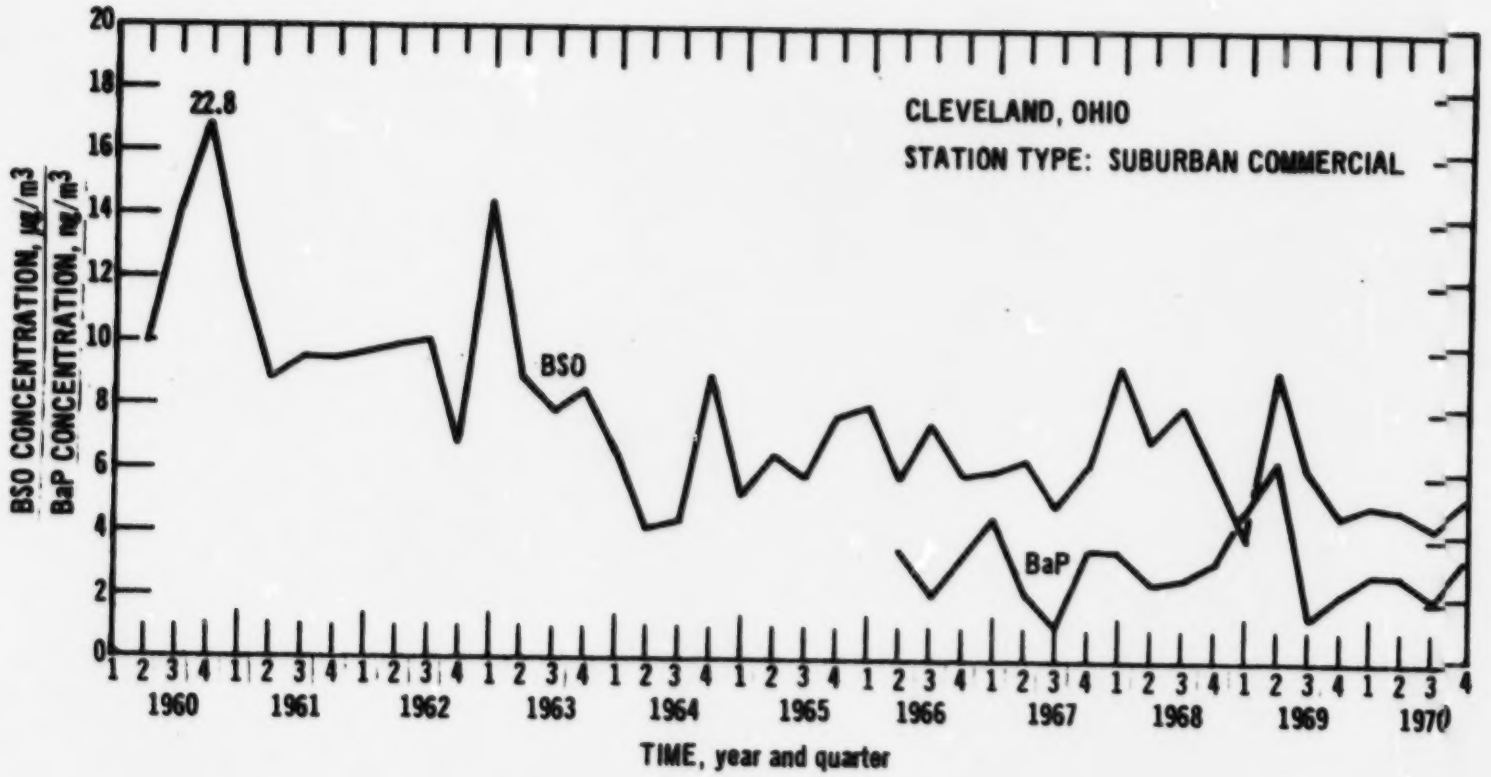

Figure 3-4. Quarterly averages of BSO and BaP at the Cleveland, Ohio NASN Station.

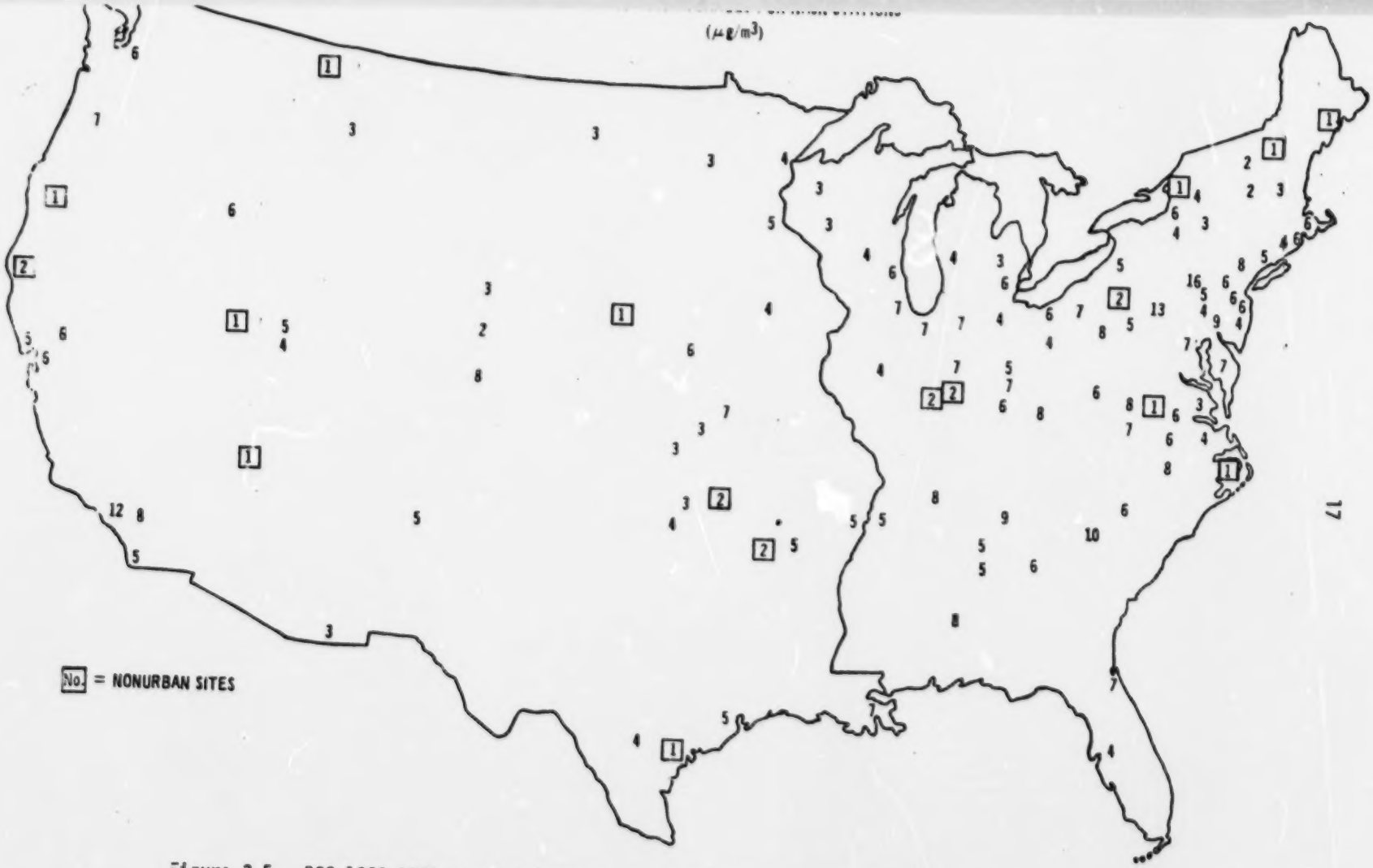

Figure 3-5. BSO 1968-1970 Rounded Averages for NASN Stations Having Complete Data For the 3 Years Considered. Averages Enclosed By ◘ Represent Nonurban Stations.

3.2.3. Geographical Concentration Across the United States

Figure 3-5 presents BSO average concentration for the most recent 3 year period (1968-1970) where NASN data is available. Stations are not included on this map which had incomplete or missing data for one or more of the years considered. The data presented here do not provide a complete assessment of spacial variations of BSO because of the large gaps in the coverage especially in the Western United States. However, there is enough coverage to compare broad sectors of the country. The averages enclosed by squares represent nonurban stations.

Average concentrations of BSO do not exhibit any clear differences between various sectors of the country. The median of the urban station averages is slightly higher for the eastern sites being approximately 6ug/m^3 as opposed to about 5 ug/m^3 for the western sites. The percentage occurrence of station averages above 8 ug/m^3 is about the same between eastern and western sites. The highest 1968-1970 BSO averages of 16 and 13 ug/m^3 both occur in Pennsylvania in Scranton and Altoona respectively, where coal is still used quite extensively for heating and other purposes.

Overall data at urban and nonurban stations point to the generation of BSO by a fairly ubiquitous group of sources across the country. Since the individual hydrocarbons which comprise the BSO fraction are generated by such a large number of diverse stationary and mobile sources, it is not surprising that geographical differences in source emissions may be hidden because of the general nature of the measurement. Larger differences in this fraction between various regions of the country may have been more evident if more data were available when the contribution from the combustion of coal for residential and commercial heating was much greater.

3.3. Trends in Benzo(a)pyrene

3.3.1. National Urban and Nonurban Trends

Benzo(a)pyrene, like the BSO fraction, shows a similar decrease in the composite average of the 32 urban stations over the period 1966-1970. Figure 3-6 shows composite station BaP averages for the period 1966-1970. The average BaP concentration decreased from 3.1 nanograms/m^3 in 1966 to 2.1 nanograms/m^3 in 1970, a decrease of approximately 30 percent. The trends in BaP concentrations over the time period 1966-1970 show 17 out of 32 sites with a decreasing trend pattern, while the remainder do not exhibit any trend one way or the other. Statistical significance of the BaP trends could not be determined because of the limited number of years of data available. (Appendix A gives a description of the trends at the individual stations.) Sites having little winter heating demand generally showed a pattern of no trend, as did some sites with a heavy heating demand such as those in Minneapolis and Chicago. In summary, the nonurban average has declined slightly during the 5-year period 1966-1970.

It is unfortunate that pre-1966 BaP data are not available at these sites. It would have been extremely interesting to see if the BaP pattern would have resembled the trend in BSO for the period 1960-1964, which represented the period of greatest change. As an alternative comparison, seven sites were examined which had 1958 and 1959 BaP data that could be compared with 1966-1970 data. A drop in BaP concentrations was found at 6 of the 7 stations. The most frequent decrease was 50 percent between the two time periods, whereas the largest decrease was

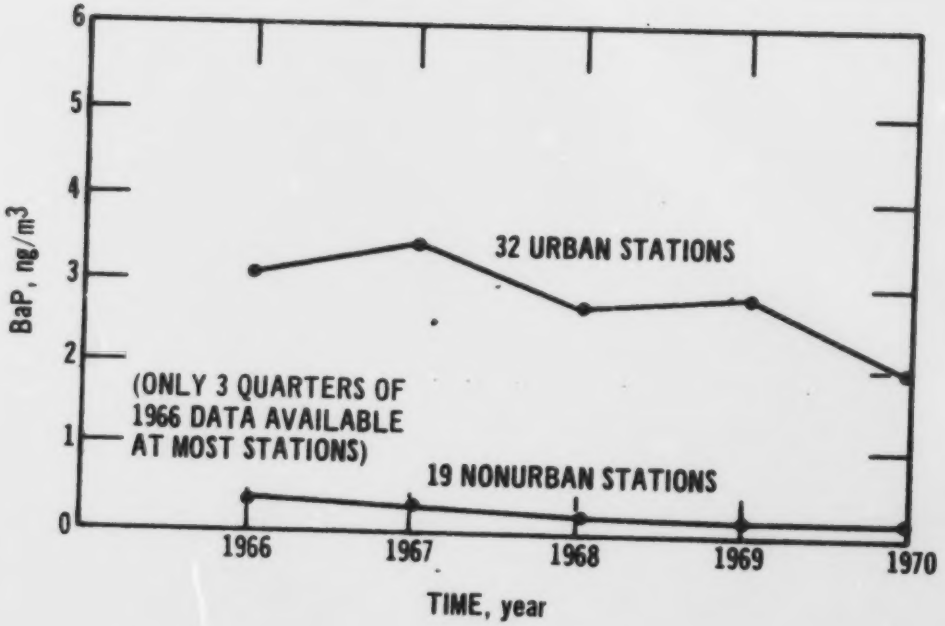

Figure 3-6. Composite annual average of BaP concentrations for 32 urban and 19 nonurban NASN stations.

was 90 percent. The study by the National Academy of Sciences on Particulate Polycyclic Organic Matter[3] states that average BaP concentrations in U. S. cities have decreased since 1950 by a factor of about 3.

The rank correlations for BaP like those for BSO are mostly negative (Table 3-2). Of the 126 stations studied for BaP over the 5 year period (1966-1970), 105 stations had negative coefficients of annual average BaP versus time. These negative correlations resulted primarily from the fact that 1970 was the low year in terms of BaP for a vast majority of the stations studied. An explanation for the drop in 1970 is not known. Significance levels were not computed for BaP because there were not enough years of data for this test to be meaningful. Again, now for BaP the majority of the nonurban sites are found to have negative trend correlations (13 out of 22).

3.3.2. Seasonal Trends

Concentrations of BaP also exhibit a seasonality as shown in Figure 3-7. Average BaP concentrations for the heating season exceed those of the non-heating season by a factor of approximately 2 or 3. The BaP seasonality for the Cleveland NASN data (Figure 3-4) does not follow the general high winter-low summer concentration pattern. This could be the result of contribution of significant industrial emissions of BaP being produced uniformly throughout the year.

3.3.3. Geographical Concentration Across the United States

Average 1968-1970 BaP concentrations in nanograms/m^3 are shown in Figure 3-8. The averages are superimposed upon a map of the United States showing four categories of bituminous and lignite coal distribu-

Table 3-2. Distribution of Spearman Rank Correlation Coefficients of BaP (1967-1970) Versus Time for Urban and Nonurban NASN Sampling Sites

Spearman Rank Correlation Coefficient Categories	Benzo(a)pyrene Urban Sites	Benzo(a)pyrene Nonurban Sites
-0.81 to -1.0	39	1
-0.61 to -0.80	15	3
-0.41 to -0.60	24	3
-0.21 to -0.40	13	2
<0.00 to -0.20	12	4
0	2	2
>0.00 to +0.20	0	0
+0.21 to +0.40	5	4
+0.41 to +0.60	12	1
+0.61 to +0.80	2	1
+0.81 to +1.00	2	1
TOTAL	126	22

tion by state. It is presumed that the coal is primarily distributed to the smaller users within the states, such as commerical and residential establishments for heating purposes. The averages enclosed by a square represent nonurban NASN locations.

Average concentrations of BaP show a distinct gradient from higher concentrations in the East to lower concentrations in the West consistent with the overall pattern of retail coal distribution. Generally speaking, the association between average concentrations of BaP and coal distribution is fairly strong with higher concentrations (4 nanograms/m^3 or more) occurring almost exclusively in the two highest coal categories, i.e. for states having greater than 100,000 tons of coal. Sampling sites having low average BaP concentration in high coal distribution states perhaps could result from the site being in a poor location with respect to sources of BaP or the specific city is not a heavy user of coal in contrast to other cities in the state.

The median of the station averages was approximately double for the eastern stations (2 nanograms/m^3) than the western stations (1 nanogram/m^3). There was not a single occurrence of western station average exceeding 3 nanograms/m^3 while 16 eastern stations had averages either equal to or in excess of 4 nanograms/m^3. The majority of these high eastern stations were situated in the States of South Carolina, North Carolina, Virginia and the more heavily industrialized cities of Tennessee, Kentucky, West Virginia, Pennsylvania, New York, Michigan and Wisconsin. It is interesting that BaP concentrations are relatively low in the extreme northeastern portion of the

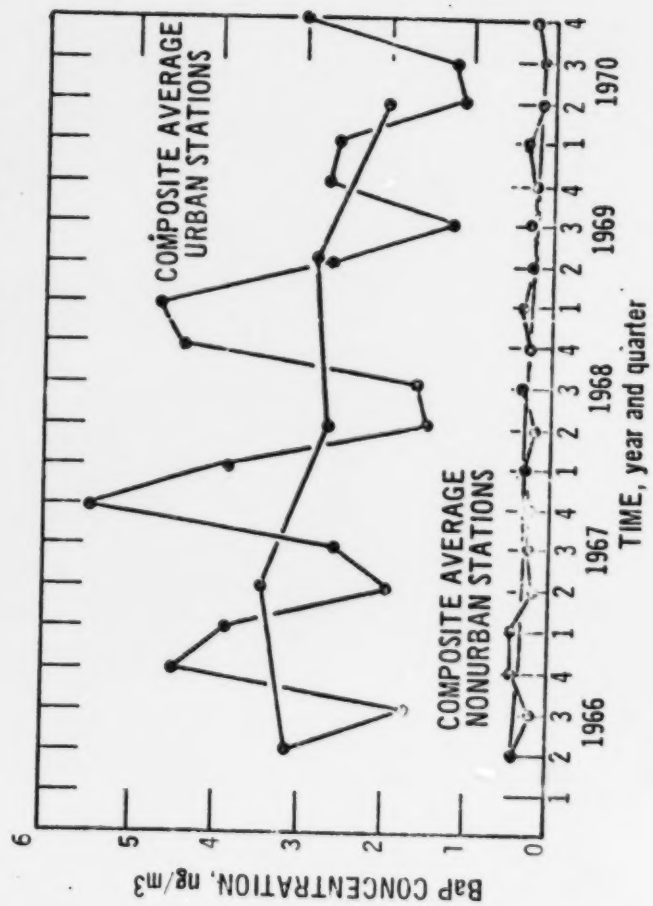

Figure 3-7. Composite Quarterly Averages for BaP at 32 Urban and 19 Nonurban NASN Stations.

country including the New York City-New Jersey area and in Los Angeles where high concentrations of BSO have been observed. Los Angeles BaP concentrations no doubt come about from the relatively small heating demand and the effect of possibly other pollution control practices designed to reduce emissions of aromatic hydrocarbons. Another possible contributing factor to the Los Angeles BaP concentrations observed is the atmospheric destruction of BaP by products of photochemical reactions e.g. ozone. At this time knowledge is lacking concerning the destruction of BaP and other hydrocarbons by this mechanism. The nonurban stations with the exception of the site in Glacier National Park in Montana (0.4 Ng/m^3) generally show an east to west concentration gradient from higher to lower concentrations consistent with the results found for the urban stations.

3.4. Analysis of 1971 and 1972 BSO and BaP Data

3.4.1. Analysis of 1971 and 1972 NASN Data

Chemical analysis of the NASN samples for BSO and BaP was last done on a network basis for 1970. Recently new analyses have been performed on a selected group of 33 NASN stations for the years 1971 and 1972 thereby making it possible to examine these data for trends through 1972. For the most part these new data are from cities where significant industrial sources of particulate hydrocarbons are present.

The trends at the individual stations through 1972, where enough data is available, is predominantly decreasing for both BSO and BaP. Appendix C provides a description of the trends at the 33 sites. It should be noted that the minimum annual average per site

Figure 3-8. BaP 1968-1970 Rounded Average for NASN Stations Having Complete Data for the 3 Year Period Considered and 1970.

for BSO and especially BaP occurred for the most part in either 1971 or 1972. In no case did the minimum average occur for either measurement earlier than 1969.

A comparison of the frequency distribution of annual averages over the period 1967 to 1972 is shown in Figure 3-9. This summary represents a different sample of stations for each year because all stations did not have data for every year considered in this analysis. The stations included in this summary are those given in Appendix C. The 1971 data was the least complete with only 19 of the 33 stations having a representative annual average. It is fortunate that the 1972 data is fairly complete allowing reasonable comparisons between it and the earlier years. The distributions of BSO and especially BaP show a shift over the period to higher frequencies at lower average concentration. The BSO median of the station annual averages represented for each year decreased from 6.3 ug/m^3 in 1967 to 4.0 ug/m^3 in 1972, whereas the BaP median dropped from 3.0 nanograms/m^3 to 0.9 nanograms/m^3 over this same period. Therefore based on these admittedly limited recent data, the decreasing trends in BSO and BaP have appeared to continue through 1972 at urban center-city locations.

3.4.2. Analysis of Denver Multi-site BSO Data

Thus far the trends which have been observed in the BSO fraction pertain almost exclusively to center city commercial areas because of the location of the NASN sampling sites. However, in the Denver metropolitan area additional BSO data was measured by the state in the suburban and outlying areas where trends can be evaluated.

FIGURE 3-9. PERCENTAGE FREQUENCIES OF SPECIAL STUDY BSO AND BaP FOR YEARS 1967-1972, INCLUDING THE 50TH (STRAIGHT VERTICAL LINE) AND 90TH (DASHED VERTICAL LINE) PERCENTILES OF THE INDIVIDUAL STATION AVERAGES BY YEAR.

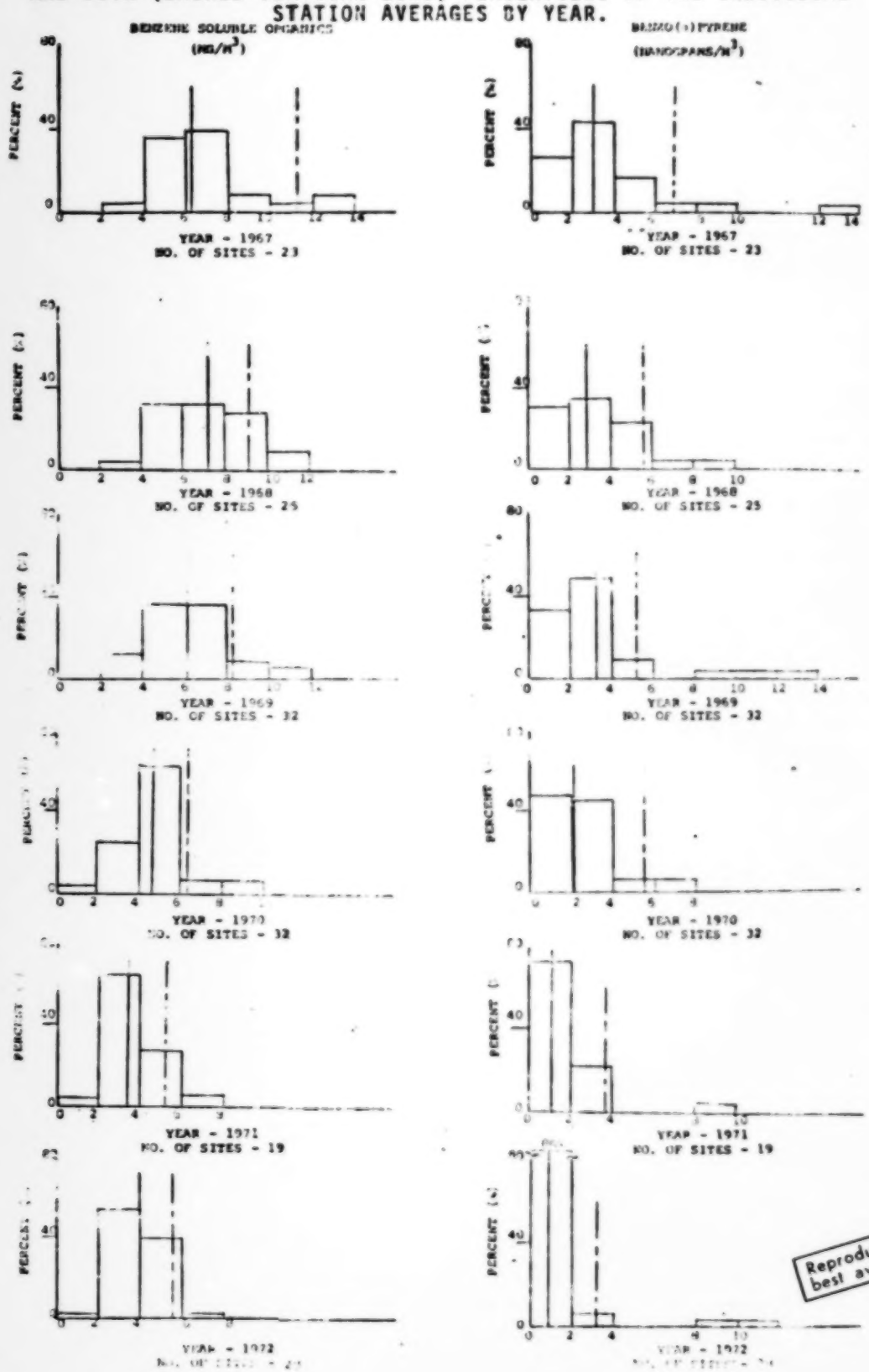

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FIGURE 3-10. COMPARISON OF BSO TRENDS FOR 6 STATIONS IN THE DENVER METROPOLITAN AREA

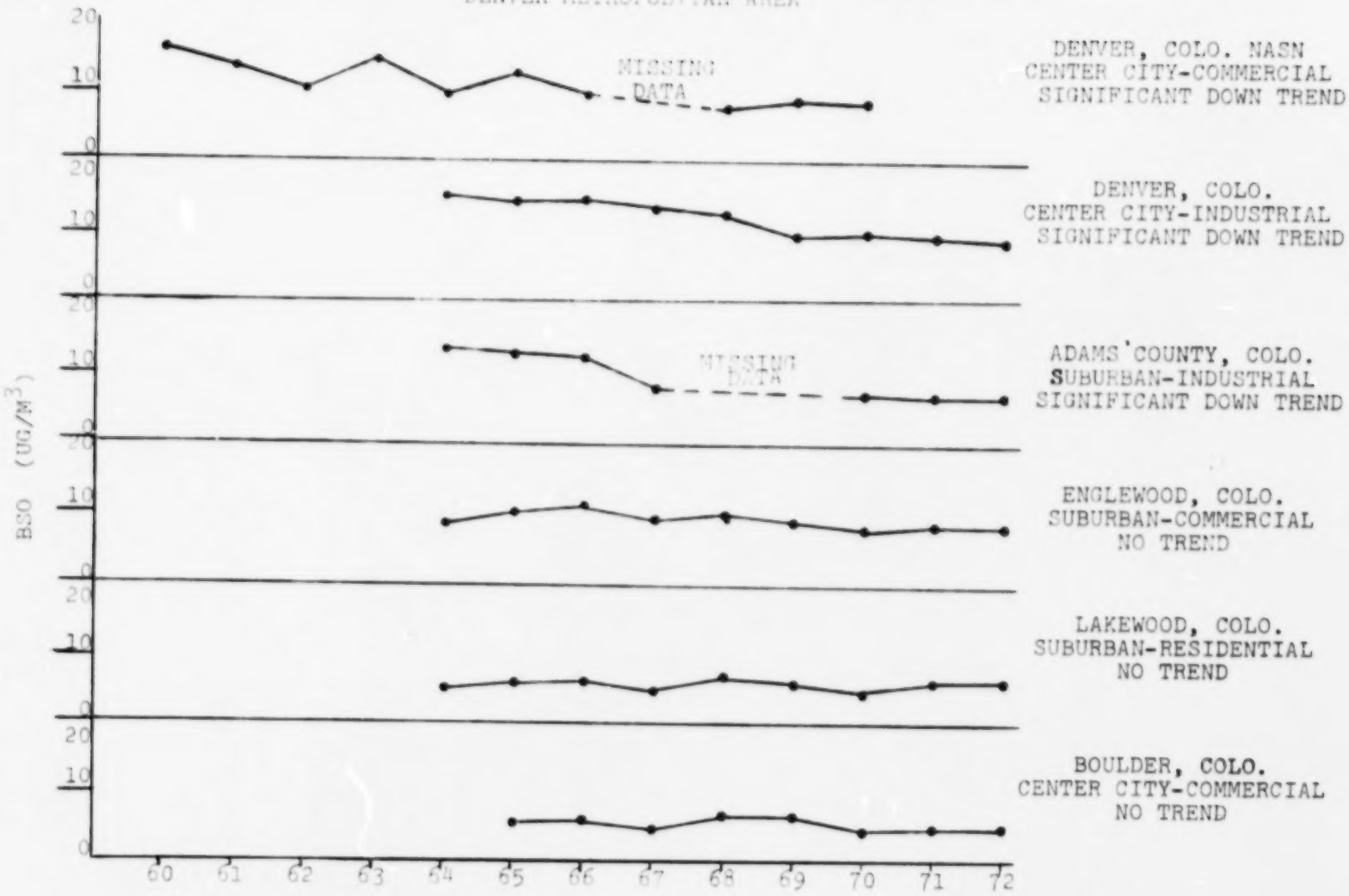

Figure 3-10 presents annual averages for six sites in the Denver area. The Denver NASN site follows the general pattern discussed before by most center city NASN sites, that is a decreasing pattern dropping from almost 16 ug/m^3 in 1970 to about 8 ug/m^3 in 1970. The very irregular pattern, for at least the first half of the data record shown by the annual averages at this site suggest the influence of a powerful local point source which given the proper meteorological conditions will effect the sampling site.

The state sites which generally cover the period 1964 through 1972 exhibit different trend patterns in some cases. The state site located in the city and classified as center city-industrial shows a significant trend downward for the period 1964-1972, similar to the NASN sity. The site in Adams County, which is classified as a suburban-industrial site, shows BSO concentrations falling very abruptly in 1967 and continuing to fall slightly for the remainder of the data record. Sufficient data for the years 1968 and 1969 were not available so that annual averages could be estimated for this site. The abrupt shift at this site probably reflects a real reduction in emissions of hydrocarbon compounds near this site. Concentrations of total suspended particulate matter appear to have fallen after 1966 along with the BSO. Also the seasonal pattern in BSO concentrations appears to be dampered after the data record starts up again in 1970. Of the remaining 3 sites, the Englewood site (suburban-commercial) has the highest BSO concentration following roughly the pattern observed at the NASN station through 1970. The Lakewood site, classified as suburban-residential, has lower BSO

concentration than the sites already mentioned. The year to year average concentrations have remained essentially the same for the years where data is available. The Boulder site although removed from the immediate Denver area follows almost exactly the average concentration curve of the Lakewood station. These data appear to suggest that trends in organic particulate concentrations in non center city locations may not be decreasing as is the case for the center city sites. Much more data is needed before an accurate assessment of trends in BSO and BaP at sites other than center-city can be made.

3.5. Trends Comparison with National Coal Consumption

The results of this analysis thus far have shown a very pronounced decrease in benzene-soluble organic fraction over the period 1960-1970 at numerous NASN stations. At most of the stations studied (118 out of 126), the available data indicated a decreasing pattern of BSO with time. Seventy-five of the 118 stations with negative correlations had coefficients that were statistically significant. These stations could be said to possess a downward trend.

It is very difficult to assign specific causes to the BSO and BaP trends because of the wide variety of sources producing these airborne particulates. Also, because of the passage of time, it is impossible to reconstruct local source-sampler configurations that could have impacted on these patterns. Nevertheless, some general remarks concerning probable changes in air pollution sources that affect the downtown or business areas may be helpful.

Table 3-3 shows a breakdown of 1968 nationwide emissions of BaP,[3]

which is a gross indicator of emissions of other polycyclic aromatic hydrocarbons. Emission estimates by source category are not available for the total benzene-soluble organics because of the countless individual organic compounds present in this fraction. However, since the aromatics comprise a major portion of the total fraction, it can be assumed that the major sources given for BaP also apply to the BSO fraction. The largest single source of BaP is attributed to the rather inefficient combustion of coal in residential furnaces. This is strongly contrasted with coal used in steam electric utilities, wherein total BaP emissions represent less than 0.1 percent of the total. The other major sources of BaP in urban areas are: wood burning (40 tons per year); enclosed incineration (33 tons per year); vehicular (32 tons per year); and in certain areas industrial (200 tons per year), depending upon the type of industry and its proximity to the main urban area. Coal refuse fires (340 tons per year) and forest and agricultural burning (140 tons per year) are major sources, but their contribution to urban concentrations of BaP would be relatively minor because of their remoteness from the urban area. Thus, the major sources of BaP emissions likely to be present in all urban areas that have a major impact on concentrations of BaP and BSO monitored at the center-city oriented NASN stations are those from residential coal combustion, enclosed incineration, urban open burning, and vehicular travel.

Figure 3-11 shows the annual national consumption of bituminous and lignite coal for the Bureau of Mines category "Retail Delivered to Other Consumers"[4] (assumed to be primarily small consumers such as homes,

Table 3-3. Estimated 1968 BaP Emissions In The United States

Source Category	Emissions (Tons/Year)
Heat and Power Generation	
Coal	
Residential Furnaces	420
Intermediate Units (Commercial)	10
Steam Power Plants	1
Oil	2
Gas	2
Wood	40
Refuse Burning	
Enclosed Incineration	33
Open Burning	
Coal Refuse Fires	340
Forest and Agricultural	140
Other (Vehicle Disposal, Domestic, Commercial and Industrial Burning)	74
Industrial	~200
Vehicular	32
TOTAL	~1300

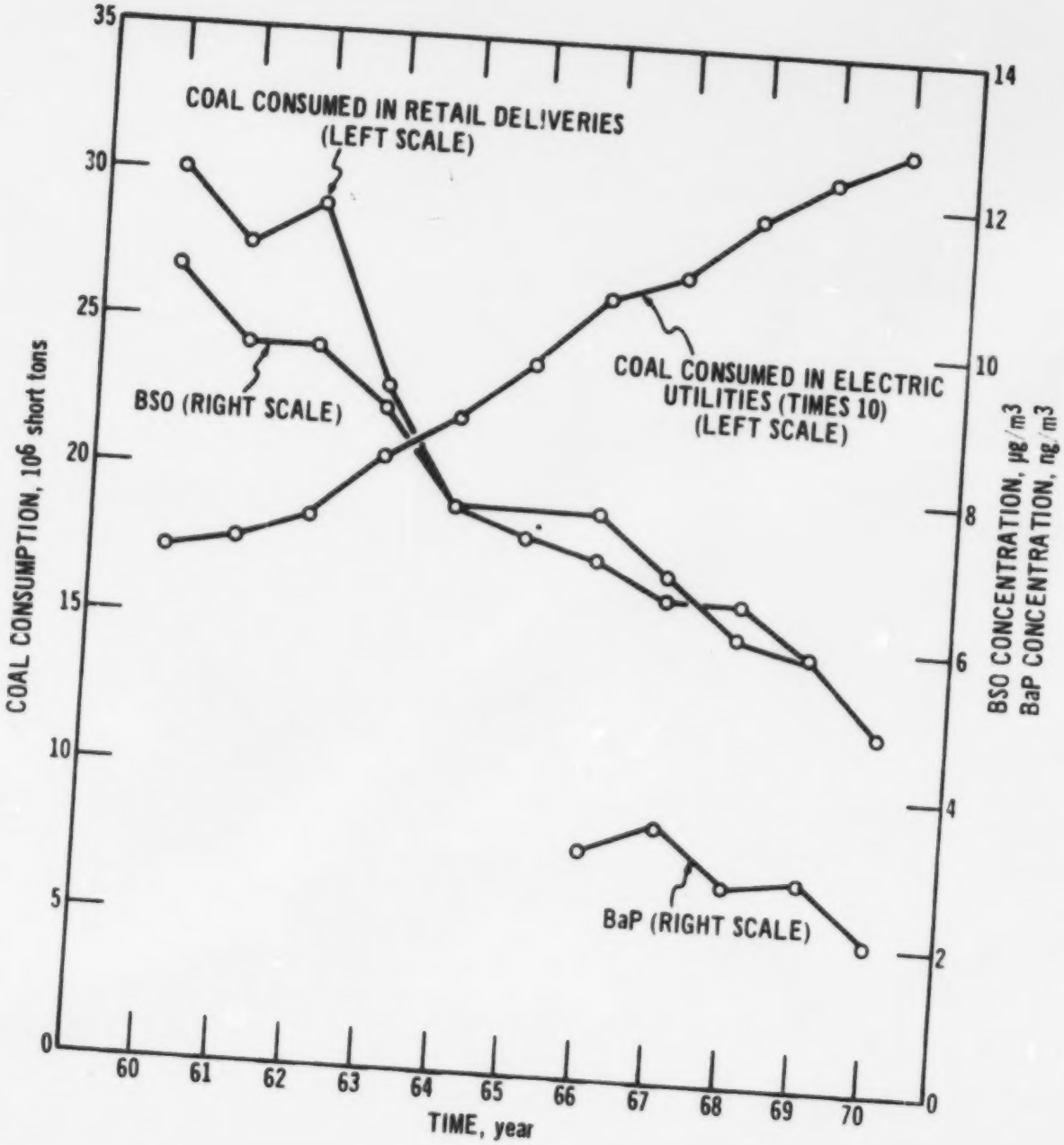

Figure 3-11. Trends in national coal consumption, BSO and BaP annual averages.

apartments, and office buildings) versus the urban composite annual average BSO and BaP concentrations. Eliminating the 4 or 5 stations from the group of 32 for which the use of coal for residential and commercial heating is nonexistent or minimal did not greatly affect the composite average. These overall patterns for coal consumption and composite average BSO concentrations are very similar, each of which in 1970 is approximately one-half of the 1960 value. Also shown on this graph is the trend in coal consumption for steam-electric power plants. Even though the usage of coal in electric utilities has about doubled from 1960 to 1970, its effect upon center-city concentrations of BaP and BSO is generally minor. The two factors that account for this are: (1) the combustion process in power plants is more efficient, resulting in lower emissions of hydrocarbons, and (2) usually the larger electric generating plants are located outside the main urban area. The reduction in the usage of residential coal appears to be the single greatest factor leading to the downward trends seen for these two pollutants.

Another factor that has likely contributed to this downward trend has been the enforcement of regulations to control smoke emissions in most large metropolitan areas. In addition, there has been a trend toward the elimination of open burning and utilization of more efficient combustion technology for solid-waste disposal.

If pre-1966 BaP data were available, a better assessment of the impact that the shift from coal to other fuels had on the ambient concentrations of the polycyclic organic matter could be made. However, it is indeed possible that ambient BaP and BSO concentrations were much higher during the 1940's and 1950's, paralleling the trend in retail coal consumption.

APPENDIX A

Urban Sites Used in Composite Analysis

	NASN Station	Trend Description BSO (1960-1970)	BaP (1967-1970)**
1.	Tucson, Arizona	Decreasing*	Decreasing
2.	Los Angeles, Calif.	Decreasing*	No Trend
3.	San Francisco, Calif.	Decreasing*	Decreasing
4.	Hartford, Conn.	Decreasing*	Decreasing
5.	New Haven, Conn.	Decreasing*	Decreasing
6.	Atlanta, Georgia	Decreasing*	Decreasing
7.	Honolulu, Hawaii	Decreasing*	No Trend
8.	Chicago, Ill.	Decreasing*	No Trend
9.	Indianapolis, Ind.	Decreasing*	Decreasing
10.	Des Moines, Iowa	Decreasing*	Decreasing
11.	Wichita, Kansas	Decreasing*	No Trend
12.	Baltimore, Md.	Decreasing*	Decreasing
13.	Detroit, Mich.	Decreasing*	Decreasing
14.	Minneapolis, Minn.	Decreasing*	No Trend
15.	St. Paul, Minn.	Decreasing*	Decreasing
16.	Helena, Montana	Increasing	Decreasing
17.	Albuquerque, N.M.	Decreasing*	Decreasing
18.	Cincinnati, Ohio	Decreasing*	No Trend
19.	Cleveland, Ohio	Decreasing*	No Trend
20.	Columbus, Ohio	Decreasing*	No Trend
21.	Youngstown, Ohio	Decreasing*	No Trend
22.	Portland, Oregon	No Trend	Decreasing
23.	Philadelphia, Pa.	Decreasing*	Decreasing
24.	Pittsburgh, Pa.	Decreasing*	No Trend
25.	Providence, R.I.	Decreasing	No Trend
26.	Chattanooga, Tenn.	Decreasing*	Decreasing
27.	Nashville, Tenn.	Decreasing*	Decreasing
28.	Houston, Texas	Decreasing*	No Trend
29.	Salt Lake City, Utah	Decreasing*	No Trend
30.	Seattle, Wash.	Decreasing	No Trend
31.	Charleston, W. Va.	Decreasing*	No Trend
32.	Milwaukee, Wis.	Decreasing	Decreasing

* Trends at these sites were judged to be statistically significant at the α=.05 level of significance.

** Trends in BaP concentrations were not tested for significance because of the insufficient number of years of data available.

APPENDIX B

Nonurban Sites Used in Composite Analysis

NASN Station	Trend Description	
	BSO (1965-1970)	BaP (1967-1970)**
1. Grand Canyon Natl. Park, Ariz.	Decreasing	Decreasing
2. Montgomery County, Ark.	Decreasing	No Trend
3. Humboldt County, Calif.	No Trend	No Trend
4. Monroe County, Ind.	Decreasing	Decreasing
5. Parke County, Ind.	No Trend	No Trend
6. Acadia Natl. Park, Maine	Decreasing	No Trend
7. Glacier Natl. Park, Mont.	No Trend	No Trend
8. Thomas County, Nebraska	Decreasing	No Trend
9. White Pine County, Nev.	No Trend	No Trend
10. Coos County, N. H.	No Trend	Decreasing
11. Jefferson County, N. Y.	No Trend	No Trend
12. Cape Hatteras, N. C.	No Trend	No Trend
13. Cherokee County, Okla.	No Trend	No Trend
14. Curry County, Oregon	Decreasing*	No Trend
15. Clarion County, Pa.	No Trend	No Trend
16. Black Hills Natl. Forest, S. D.	No Trend	No Trend
17. Matagorda County, Texas	No Trend	Increasing
18. Orange County, Vermont	No Trend	Decreasing
19. Shenandoah Natl. Park, Va.	No Trend	No Trend

* Trends at these sites were judged to be statistically significant at the α=.05 level of significance.

** Trends in BaP concentrations were not tested for significance because of the insufficient number of years of data available.

APPENDIX C

Trends at Sites Included in 1971 and 1972 Special Analysis for BSO and BaP

	NASN Station	Trend Description (Data Through 1972) BSO	BaP
1.	Gadsden, Alabama	Decreasing*	Decreasing
2.	Montgomery, Alabama	Decreasing*	Decreasing*
3.	Jacksonville, Florida	Decreasing	Decreasing*
4.	Honolulu, Hawaii	Decreasing*	Decreasing
5.	Chicago, Illinois	Decreasing*	Decreasing
6.	Gary, Indiana	Insufficient Data	Insufficient Data
7.	Hammond, Indiana	Decreasing	No Trend
8.	Indianapolis, Indiana	Decreasing*	Decreasing
9.	Terre Haute, Indiana	Decreasing*	Insufficient Data
10.	Ashland, Kentucky	Decreasing	Decreasing
11.	Baton Rouge, Louisiana	Decreasing*	Insufficient Data
12.	New Orleans, Louisiana	Decreasing*	Decreasing*
13.	Baltimore, Maryland	Decreasing*	Decreasing*
14.	Detroit, Michigan	Decreasing*	Decreasing*
15.	Trenton, Michigan	Decreasing*	Decreasing*
16.	St. Paul, Minnesota	Decreasing*	Decreasing*
17.	St. Louis, Missouri	Decreasing*	Insufficient Data
18.	Buffalo, New York	Insufficient Data	Insufficient Data
19.	New York City, New York	Decreasing*	Insufficient Data
20.	Cleveland, Ohio	Decreasing*	Insufficient Data
21.	Toledo, Ohio	Decreasing*	Insufficient Data
22.	Youngstown, Ohio	Decreasing*	Decreasing
23.	Bethlehem, Pennsylvania	Decreasing	Decreasing
24.	Philadelphia, Pennsylvania	Decreasing*	Decreasing*
25.	Pittsburgh, Pennsylvania	Decreasing*	No Trend
26.	Chattanooga, Tennessee	Decreasing*	Insufficient Data
27.	Houston, Texas	Decreasing*	Decreasing
28.	Newport News, Virginia	Insufficient Data	Insufficient Data
29.	Norfolk, Virginia	Decreasing*	Decreasing*
30.	Seattle, Washington	Decreasing*	Decreasing*
31.	Spokane, Washington	Decreasing*	Insufficient Data
32.	Charleston, West Virginia	Decreasing*	Decreasing
33.	Milwaukee, Wisconsin	Decreasing*	Decreasing*

* Trends at these sites were judged to be statistically significant at the α=0.05 level of significance

** Insufficient data is noted when a site has less than 5 complete years of data.

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